

REACTION CHARACTERISTICS AND MECHANISM OF RESIDUUM HYDROCRACKING

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ABSTRACT

The Gudao vacuum residuum (GDVR) was hydrocracked in a 100 mL autoclave with crushed commercial Ni-Mo Catalyst within a temperature range of 390-420°C. The characteristics of series reaction remains obviously in the residuum hydrocracking. The relationship of coke yield and conversion for catalytic hydrocracking is different from thermal cracking and non-catalytic hydrocracking. The presence of catalyst and hydrogen can significantly inhibit the coking reaction, but simultaneously decreases the cracking rate to a certain extent. The apparent activation energy of residuum catalytic hydrocracking is close to that for thermal cracking. It can be derived that rate limiting step of the residuum catalytic hydrocracking is essentially thermal activation.

INTRODUCTION

The residuum hydrocracking is a very complex reaction system because the feed and product contain innumerable compounds and various reactions occur simultaneously. So it is difficult to study kinetics for every component in this system. Catalytic hydrocracking is more complicated than the non-catalytic hydrocracking. In residuum hydrocracking there often exist three phases of gaseous, liquid, and solid. The catalytic reactions occur on the surface of catalyst and the thermal reactions take place in the interspace of catalyst particles. The reactions not only occur in the liquid phase, but also happen in gaseous phase. Residuum thermal cracking is a free radical chain reaction, but there are different views for the mechanism of heavy oil catalytic hydrocracking due to the various feed, catalysts, and method used by different investigators.

Through the comparison of the chemical analogies of visbreaking, hydro-thermal cracking, catalytic cracking and catalytic hydrocracking, Le Page^[1-2] found that the driving force of the conversion reactions is essentially thermal activation in the temperature range applied. The catalyst, the hydrogen present, and the sophistication of the various techniques are merely expediences, which basically participate in limiting, indeed controlling, the condensation side reactions involving the heavy resin and asphaltene molecules.

De Jong^[3] (1994) investigated the hydroconversion of heavy vacuum gas oil in a trickle-bed reactor at about 450°C and moderate hydrogen pressure (30atm). He found that the cracking reactions are hardly affected by the presence of the metal active component of the catalyst and thought the cracking reactions are not acid-catalyzed but mainly thermally induced under the prevailing conditions. Through the studies of atmospheric residuum^[4], it is observed that catalytic cracking and thermal cracking take place simultaneously, the lighter distillates are mainly produced from the thermal cracking and the effect of catalyst is to offer active hydrogen to the heavy component in order to controlling coking. That is to say, the hydrogen captured by the light component come directly from the heavy component (the large molecule to be hydrocracked).

In the kinetic model of hydrocracking developed by De Jong^[5], the vapor-liquid equilibrium of the reaction mixture was considered. For fitting the experimental data, it was assumed that the cracking of molecules in the vapor phase is 25 times faster than for those present in the liquid phase. In other words it seems as if activated hydrogen in the liquid phase inhibit the radical cracking reaction, while the acceleration is apparent in the vapor phase. This assumption is in line with comments in the investigation of Sanhanen^[6] and Shabtai^[7]. The residuum hydrocracking made by Xu^[8] showed that the conversion of catalytic hydrocracking is greater than that of non-catalytic hydrocracking, which is ascribed to the inhibition of a great number of active hydrogen on the polymerization and coking reactions involving the heavy components.

As a whole, the recognition for heavy oil catalytic hydrocracking has been being semi-theoretical and no consistent conclusion has been drawn about the reaction mechanism and the effect of catalyst and hydrogen. For instance, active hydrogen capturing the large molecular radical can inhibit coking reaction and will be of help for enhancing the distillate yields, but the cracking rate will be decreased and distillate yield declined when the small and medium radicals are captured. The final result would depend upon the concrete situations. In the present paper, hydrocracking characteristics of GDVR will be investigated and the reaction mechanism discussed.

EXPERIMENTAL

The Gudao vacuum residuum was hydrocracked in a 100mL autoclave with crushed ICR-130H Catalyst of 0.35mm average diameter at the initial hydrogen pressure 8.5 MPa, with agitation speed at 850rpm and in the temperature range of 390-420. After hydrocracking, gas, liquid and coke were separated and analyzed. The yield of gas, liquid and coke were determined and the simulated distillation data of feed and liquid product were obtained.

RESULTS AND DISCUSSION

Product Distribution of GDVR Hydrocracking

The yields of gasoline and diesel increase gradually with the reaction time. The increasing rate is slow at the initial period of reaction and become faster and faster toward the end of reaction. The yield of vacuum gas oil (VGO) increases firstly at a faster rate and then slackens gradually. It passes through a maximum at certain time and then declines slowly. The phenomena mentioned above shows that residuum hydrocracking has an obvious characteristic of series reaction. The gas yield increase gradually with time at constant temperature except in the case of 390°C. The coke yield increase quickly at the initial period and slowly with increasing reaction time.

The relationships of product yields and conversions are showed in figure 1. Gas, gasoline and diesel increases gradually with the conversion of >500°C portion, and the increasing rate is slow when the conversion is lower and becomes faster with the increase of conversion. This is because the heavy distillate must be cracked at first into middle distillate and the formation rate of light distillates becomes gradually faster with the increase of middle distillate. The middle distillate content increases at first and reaches to a maximum at a certain conversion, and then decreases gradually.

The relationship of coke yield and conversion for catalytic hydrocracking is obviously different from thermal cracking and non-catalytic hydrocracking^[9-12]. For the latter two cases the coke yield increases slowly at the initial period and grows seriously when the conversion passes a critical value (about 55—65% for GDVR), which is similar as the relationship of gas yield

versus conversion in figure 1. For residuum hydrocracking, the coke yield increases quickly when the conversion is low, and the increasing rate slows down gradually with further conversion, which is consistent with the conclusion derived by most investigators on catalyst deactivation. For the present study, the initial quickly coking may be caused by the promotion of acid catalysis on the surface of catalyst, and the hydrogenation function becomes stronger relative the cracking function when the acid sites are gradually covered by the deposition of coke, which can inhibit greatly the coking reaction.

The product selectivity versus conversion of $>500^{\circ}\text{C}$ portion is illustrated in figure 2. The selectivity of gasoline and diesel increase gradually with the conversion. The selectivity of VGO reaches a maximum at 30% conversion and then decrease gradually. The selectivities of gas and coke decrease seriously at a low conversion range and then tend to a constant. Therefore, residuum catalytic hydrocracking differs from thermal cracking and hydrocracking mainly in serious inhibition of coking and gas formation. The data points of selectivity of gas and coke versus conversion at different temperatures all fall on the corresponding curves respectively. This supports that the temperature has no effect on the selectivity of gas and coke at the conditions used in this study.

Simple kinetic model of GDVR hydrocracking

Whether the driving force of residuum catalytic hydrocracking is essentially the thermal activation can be checked by comparing the activation energy of catalytic cracking with that of thermal cracking. Residuum hydrocracking has ever been described successfully by simple first-order or second-order kinetics. The experimental results have been correlated in terms of the simple kinetic equations, with the plots of $\ln[1/(1-x)]$ and $x/(1-x)$ (x is conversion) versus reaction time, t . It is found better to describe the catalytic hydrocracking of GDVR by first-order kinetics than second-order kinetics. But the second-order kinetics is feasible

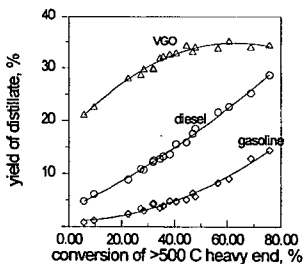


Fig.1A Yields of liquid products versus conversion

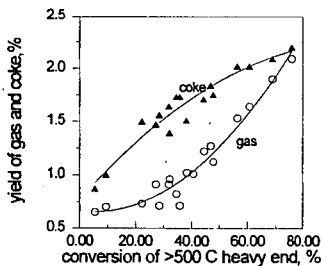


Fig.1B yield of coke and gas versus conversion

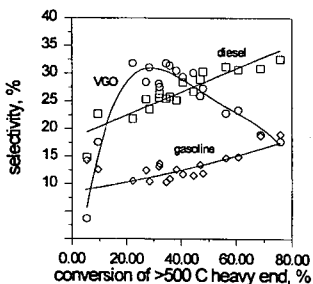


Fig.2A Selectivity of liquid products versus conversion

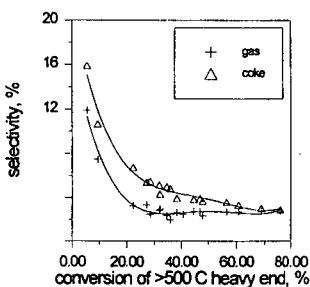


Fig.2B Selectivity of coke and gas versus conversion

when the conversion is not too high, especially for the hydroconversion of $>350^{\circ}\text{C}$ portion. It could be thought that the reaction order is affected by the lumping method when using power kinetic equations to describe hydrocracking. The rate constants (k) at different temperature were calculated according to the first-order kinetics, a linear relationship exists between $\ln(k)$ and $1/T$ (reciprocal of temperature) and the correlation coefficient is 0.9994. The activation energy of GDVR hydrocracking is listed in Table 1.

Table 1 Kinetic reactions of hydrocracking

Feed	Reaction	Catalyst	Temp($^{\circ}\text{C}$)	E (KJ/mol)	Reference
Maya VR	VR+H ₂ →Products	Dispersed Mo	397-438	~290	10
Athabasca asphaltene	Bitumen→ Products	No	370-538	130	13
Athabasca asphaltene	Bitumen→ Products	No	375-420	150	14
Huanxiling asphaltene	VR→ Products	No	385-430	260	15
Distillate	VGO+H ₂ → Products	NiW/SiAl	300-430	88.2	16
Coal tar	Tar+H ₂ → Products	NiW/SiAl	400-500	73.6	17
GDVR	VR+H ₂ → Products	No	400-420	216	18
GDVR	GDVR+H ₂ → Products	ICR130H	390-420	260-285	This work

Some kinetic results of heavy oil hydrocracking are summarized in table 1. From these results the activation energy of residuum hydrocracking in the presence of catalyst is very close to that for thermal cracking, whereas the activation energy of distillate catalytic hydrocracking is obviously smaller than that of residuum hydrocracking. This may be explained as the cracking active sites of catalyst play an important role in the distillate hydrocracking, while in the residuum catalytic hydrocracking thermal activation is predominating. The catalysts just create active hydrogen to inhibit coke deposition and simultaneously decrease the cracking rate to a certain extent.

CONCLUSION

From the present study a number of conclusions emerge.

- (1) Series reaction model is consistent with the reaction process of residuum catalytic hydrocracking.
- (2) The relationship of coke yield versus conversion is obviously different from thermal cracking and non-catalytic hydrocracking. Catalyst and hydrogen can significantly inhibit the coke deposition and simultaneously control the cracking reaction.
- (3) The initiation and rate controlling step of residuum catalytic hydrocracking is thermal activation in essence.
- (4) GDVR hydrocracking is described very well by the first-order kinetics and reaction order is affected by the lumping method.

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